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(54) Title: DETERGENT ADDITIVE GRANULATE AND METHOD FOR PRODUCTION THEREOF

(57) Abstract

The detergent additive granulate comprises a core with a primary detergent additive surrounded by a shell comprising a secondary detergent additive, a binder, and granulating agents, and optionally a filler, and a protective coating between the core and the shell, whereby the shell comprises cellulose fibres or artificial fibres, and whereby the core facultatively comprises cellulose fibres or artificial fibres. The detergent additive granulate exhibits a high physical strength, and the primary and secondary detergent additives are effectively separated from each other and/or from harmful environmental factors. The detergent additive granulate is produced by introduction of the components thereof into a granulating drum. This method of production is easily controllable and adapted for an industrial scale.

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DETERGENT ADDITIVE GRANULATE AND METHOD FOR PRODUCTION THEREOF

This invention relates to a detergent additive granulate and a method for production thereof.

The granulate according to the invention and the method for production thereof is a further development of the granulate and the method for production thereof described in Danish patent application No. 4368/88, which is carried out in a drum granulator. It is to be understood that the term drum granulator represents a broad category of granulator devices, comprising for instance pan granulators and granulation mixers.

The enzyme containing granulate described in Danish patent application No. 4368/88 comprises a core surrounded by a coating comprising cellulose fibres or artificial fibres in an amount of 1.5 to 40% by weight, based on the dry weight of the granulate except for the core, a binder in an amount of 0 to 15% by weight, based on the dry weight of the granulate, except for the core, a filler, and one or more granulating agents, whereby the core and/or the coating contains an enzyme.

The invention is a further development of the special embodiment of the invention described in Danish patent application No. 4368/88, which comprises an enzyme in either the core or the shell. However, the shell or the core in the detergent additive granulate according to the invention does not necessarily contain an enzyme; but the core contains one detergent additive (which may be an enzyme, here identified as the primary detergent additive), and the shell contains another detergent additive (which may be another enzyme, here identified as the secondary detergent additive). In those cases where the primary detergent additive should be protected against the secondary detergent additive and/or environmental factors, e.g. in cases where an enzyme is degraded by a bleaching agent and

humidity in the atmosphere, or vice versa, there is a need for an effective separation between the primary and secondary detergent additives during storage. Also, there is a need for a granulate with high physical strength, and for a corresponding method of production, which is easily controllable and adapted for an industrial scale.

Thus, the purpose of the invention is the provision of a detergent additive granulate with a high physical strength and which contains a primary and a secondary detergent additive of the above mentioned kind, wherein the primary and secondary detergent additives are effectively separated from each other and/or from harmful environmental factors, and the provision of a corresponding method of production, which is easily controllable and adapted for an industrial scale.

The detergent additive granulate according to the invention comprises a core with a primary detergent additive surrounded by a shell comprising a secondary detergent additive, a binder, and granulating agents, and optionally a filler, and a protective coating between the core and the shell, whereby the shell comprises cellulose fibres or artificial fibres, preferably in an amount of between 1.5 and 40% by weight of the shell, more preferably between 5 and 20% by weight of the shell, and whereby the core facultatively comprises cellulose fibres or artificial fibres, preferably in an amount of between 1.5 and 40% by weight of the core, more preferably between 5 and 20% by weight of the core.

Due to the protective coating between the core and the shell the two detergent additives do not harm each other during storage, and only during the application during wash the two detergent additives will be brought into contact with each other. Also, due to the content of the cellulose fibres or the artificial fibres in the shell the physical strength of the granulate is high. Furthermore, it surprisingly has been found that the granulator method of production carried out according to the guidelines indicated

in US patent no. 4,106,991, which is indicated in the previously cited Danish patent application no. 4368/88, can be easily controlled, also with two non-enzymatic detergent additives, and it can easily be adapted for an industrial scale.

EP 0 286 773 describes encapsulated enzymes, which in some regards are similar to the detergent additive granulate according to the invention in its broadest aspect. However, the prior art encapsulated enzymes do not contain reinforcing cellulose fibres or artificial fibres in the shell and is not described as being produced by means of the above indicated granulator method, but by means of the fluid bed method, which is not well adapted to production on an industrial scale.

The protective coating can be any protective coating used in the art, which do not hurt the primary or secondary detergent additives or in other manner disturb the manufacturing process or the application of the granulate. Examples of usable protective coatings are: fatty acid esters, alkoxylated alcohols, polyvinyl alcohols, ethoxylated alkylphenols, polyethylene glycols (MW 1000 to 8000), linear alcohol alkoxylates (MW 1450 to 2670), polyvinyl pyrrolidone (MW 26000 to 33000), polymeric nonylphenyl ethoxylates (MW 1975 to 4315), and dinonylphenyl ethoxylate (average MW 6900), fatty acids, e.g. palmitic acid, stearic acid, and arachidonic acid, paraffins, bee wax, waxes, mono-, di- or triglycerides of single fatty acids or mixed fatty acids, fatty alcohols, methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, and coconut monoethanol amide.

Examples of pairs of primary and secondary detergent additives are the following: (optical brightener)-(enzyme), (enzyme)-(optical brightener), (enzyme)-(bleach activator), (bleach activator)-(enzyme), (bleach activator)-(optical brightener), (optical brightener)-(bleach activator), (enzyme-chlorine scavenger), (bleach activator-chlorine scavenger), (optical brightener-chlorine

scavenger), (bleaching agent)-(enzyme), and (enzyme)-(bleaching agent).

In a preferred embodiment of the granulate according to the invention the core is of a shape corresponding to a maximum ratio between the largest and the smallest dimension of around 3, preferably around 2, more preferably around 1.5. In this embodiment a satisfactory coating around the core can always be obtained.

In a preferred embodiment of the granulate according to the invention the amount of the core is between 5 and 85% by weight, preferably between 10 and 50% by weight of the granulate, most preferably between 15 and 40% by weight of the granulate. If the amount of the core is above 85%, the loading of a sufficient amount of secondary detergent additive will be difficult, and if the amount of the core is less than 5%, the loading of a sufficient amount of primary detergent additive will be difficult.

In a preferred embodiment of the granulate according to the invention the core has a mean particle size between 100 and 1000 μm, preferably 200-700 μm. These are the particle sizes most often required by the users.

In a preferred embodiment of the granulate according to the invention the core or the shell contains an enzyme. An enzyme is a typical detergent additive which needs protection from aggressive detergent components.

In a preferred embodiment of the granulate according to the invention the enzyme is a protease, an amylase, a lipase, an amidase, a cellulase, or an oxidase. These are the most common enzymes for industrial detergent purposes.

In a preferred embodiment of the granulate according to the invention the filler consists of or comprises inorganic salts. Hereby a cheap granulate is obtained.

In a preferred embodiment of the granulate according to the invention the shell is surrounded by a final dust suppressing coating. This is advantageous in

those cases where the shell tends to produce an unacceptable amount of dust. This final dust suppressing coating can also in certain cases serve as a further protective coating.

In a preferred embodiment of the granulate according to the invention the protective coating is a mixture of a mono- and diglyceride of a fatty acid. It has been found that in this embodiment a most satisfactory protective action during the storage can be obtained. Advantageously mixtures of the kind described in Danish patent application No. 1377/88 can be used.

In a preferred embodiment of the granulate according to the invention the protective coating contains an antioxidant. Suitable examples of antioxidants or reduction agents are thiosulphates, sulfites, bisulfites, ascorbic acid, ascorbates, or butyl hydroxy toluene. In many cases an even better storage stability can be obtained due to the presence of the antioxidant.

Also, the invention comprises a method for production of the granulate according to the invention.

The method for the production of the detergent additive granulate according to the invention comprises the introduction of the core into a granulating drum, whereafter sequentially the protective coating agent, the shell material and optionally a final dust suppressing coating agent, and furthermore cellulose fibres or artificial fibres in the appropriate amounts and at the appropriate stages, are introduced into the granulating drum.

It is to be understood that any granulating drum can be used in relation to the method according to the invention. The entire process can be carried out in one of these granulating drums. Also, it is to be understood that the core can be coated with the protective coating agent in one granulating drum, whereafter the coated core can be isolated an transferred to another granulating drum for application of the shell, whereafter if wanted application

of a dust suppression coating can be performed on the same granulating drum or another granulationg drum.

The method according to the invention can be performed both batchwise and continuously.

The invention will be illustrated by the following examples.

The activity units used in the examples are defined as follows.

enzyme	activity unit	definition indicated in
proteolytic	Anson KNPU	AF 4.3/5-GB AF 220/1-GB
amylolytic	KNU	AF 215/1-GB
lipolytic	LU	AF 95/4-GB

On request these AF publications can be obtained from NOVO NORDISK A/S, Novo Allé, 2880 Bagsvaerd, Denmark.

Preparation examples

EXAMPLE 1

15 kg of a powder composition with the formulation:

15% fibrous cellulose, ARBOCEL BC 200
15% optical brightener, TINOPAL DMS-X conc. CIBA GEIGY
4% kaolin SPESWHITE ECC
12% carbohydrate binder
54% finely ground sodium sulphate

is granulated in a Lödige mixer FM 50 with pure water as granulating agent as described in US patent No. 4,106.991, Example 1.

The granulate is dried on a fluid bed to a water content below 1% and finally siftet to get a product with particle range 300 µm to 900 µm.

EXAMPLE 2

7 kg of a granulate produced as described in Example 1 with particle size between 300-900 µm is coated with a layer of glyceryl stearate/palmitate Grindtek MSP 90 (melting point 68°C) and bentonite ASB 350 ECC in the following manner.

The granulate is heated to 75-80°C in a 20 l heat jacketed Lödige mixer which temperature is kept during the whole coating process. The heated granulate is mixed and sprayed with 700 g melted MSP90 followed by a powdering with 1000 g bentonite followed by spraying with 210 g MSP90 followed by powdering with 1000 g MSP90 followed by spraying with 210 g MSP90.

The granulate is finally cooled to room temperature on a fluid bed and siftet between 300 and 1000 µm.

EXAMPLE 3

A granulate with an inner core containing an optical brightener and an outer shell containing a proteolytic enzyme with the core and the shell separated by a protective layer is produced in the following manner.

6 kg of a shell material with the composition:

2.5 kg [SAVINASE® / KNPU/g] conc. with proteolytic activity 37
0.5 kg fibrous cellulose ARBOCEL BC 200
0.6 kg carbohydrate binder
0.2 kg kaolin SPESWHITE ECC
1.2 kg finely ground sodium sulphate

is mixed and layered on the surface of 8 kg of granulate produced as described in Example 2 in a manner as described in Danish patent application No. 4368/88, Example 1, except that in the present example the core contains an optical brightener and that a 50 l Lödige mixer FM 50 was used.

The granulate is finally dried to a water content below 1% and siftet between 300 and 1000 µm.

The granulate has proteolytic activity of 6.0 KNPU/g.

EXAMPLE 4

7 kg of granulate as produced as described in Example 3 is coated with a layer of sodium thiosulphate and kaolin by a conventionel fluid bed coating process.

280 g sodium thiosulphate and 280 g kaolin SPESWHITE ECC are dissolved/dispersed in 1000 g of water and sprayed onto the 7 kg of granulate in a Glatt WSG 5 fluid bed with continuous layering and drying.

Air inlet temperature 50°C. Air outlet temperature 35°C.

The process is concluded with a 5 min. drying period with air inlet temperature 50°C.

The granulate has a proteolytic activity of 5.2 KNPU/g.

EXAMPLE 5

7 kg of granulate produced as described in Example 4 is coated with a protective coating of 280 g Grindtek MSP90 followed by 875 g titanium dioxyde: Kaolin (SPESWHITE) 1:1 followed by 140 g Grindtek MSP90 as described in example 2.

The granulate is cooled to room temperature on a fluid bed and siftet between 300 and 1000 µm.

The granulate has a proteolytic activity of 4.7 KNPU/g.

Stability test of granulates in Examples 3, 4 and 5

The stability test is made at a temperature of 37°C and a humidity of 70%.

	0 day	7 days		17 days	
Sample	KNPU/g	KNPU/g	Residual act.	KNPU/g	Residual act.
3	6.00	2.56	42.7%	2.25	37.5%
4	5.20	3.50	67.3%	2.71	52.1%
5	4.70	3.05	64.9%	2.50	53.2%

The above data indicates that the final dust suppressing and protective coating generates an increased stability.

EXAMPLE 6

14,7 of a powder composition with the formulation

2.2 kg fibrous cellulose, ARBOCEL BC 200
1.2 kg bentonite, ASB350, ECC
1.8 kg carbohydrate binder
9.5 kg TAED

was granulated in a Lödige mixer FM 50 with 3.0 kg of a 2% aqueous solution of a carbohydrate binder in the manner described in US patent No. 4,106,991, Example 1.

In a fluid bed the granulate was dried to a water content below 1% and finally siftet to obtain a product with particle range 300 µm to 900 µm.

10 kg of dry 300 - 900 µm product was subsequently coated with 8.0% of hydrogenated tallow (melting point 59°C)

and 28% kaolin, Speswhite ECC, in the manner described in Example 2, except that the tallow was applied in one single (first) step followed by powdering with kaolin.

A granulate with an inner core containing TAED and an outer shell containing a proteolytic enzyme with the core and the shell separated by a protective layer was produced in the following manner.

10 kg of the tallow coated TAED containing granulate was cooled to room temperature and then transferred to a Lödige mixer FM 50 and in a first step sprayed with 200 g PEG 300 followed by layering of 4.6 kg of shell material mixture with the composition

0.6 kg SAVINASE® concentrate, 50 KNPU/g
0.5 kg fibrous cellulose, Arbocel BC200
0.2 kg titanium dioxide
0.3 kg kaolin, Speswhite ECC
0.2 kg carbohydrate binder
2.8 kg finely ground sodium sulphate

The shell was supplied with 1.4 kg of a 28.5% aqueous solution of a carbohydrate binder in the manner described in Danish patent application No. 4368/88, Example 1, except that in the present example the core contains a perborate activator, TAED, and that a 50 l Lödige mixer was used.

The granulate was finally dried to a water content below 1% and sieved to between 300 µm and 1000 µm.

EXAMPLE 7

A TAED containing granulate coated with hydrogenated tallow was produced as described in Example 6, except that 20% kaolin was used in the wax coating step.

A granulate with an inner core containing TAED and an outer shell containing an optical brightener and with the

core and the shell separated by a protective layer was produced in the following manner.

10 kg of the tallow coated TAED containing granulate was cooled to room temperature and then transferred to a Lödige mixer FM 50 and in a first step sprayed with 200 g PEG 300 followed by layering of 4.6 kg of shell material mixture with the composition

0.75 kg optical brightener, Tinopal DMS-X, Ciba-Geigy
0.75 kg fibrous cellulose, Arbocel BC200
0.20 kg titanium dioxide
0.30 kg bentonite ASB 350, ECC
0.20 kg carbohydrate binder
2.40 kg finely ground sodium sulphate

The shell was supplied with a continuous self-regulating loss-in-weight powder dosing system with a powder dosing rate of 20 kg/h. As a total 1.4 kg of an 28.5% aqueous carbohydrate binder solution was sprayed to bind the powder to the surface of the core particles. Otherwise the layering was applied as described in PCT WO 89/08695, Example 1.

The granulate was finally dried to a water content below 1% and sieved to obtain a product with particle range 300 - 900 µm.

EXAMPLE 8

10 kg of SAVINASE® granulate with particle sizes between 300 µm and 700 µm produced as described in US 4,106,991, Example 1, except that it was based on sodium sulphate, was coated with 8% of hydrogenated tallow and 26% of kaolin, as described in Example 6.

A granulate with an inner core containing the proteolytic enzyme SAVINASE® and an outer shell containing

an optical brightener with the core and the shell separated by a protective layer, was produced in the following manner.

10 kg of the tallow coated Savinase® containing granulate was cooled to room temperature and then transferred to a Lödige mixer FM 50 and in a first step sprayed with 200 g PEG 300 followed by layering of 9.2 kg of a shell material mixture with the composition

1.5 kg optical brightener, Tinopal DMS-X, Ciba-Geigy
1.0 kg fibrous cellulose, Arbocel BC200
0.4 kg titanium dioxide
0.6 kg kaolin, Speswhite ECC
0.4 kg carbohydrate binder
5.3 kg finely ground sodium sulphate

The shell was supplied with a continuous self-regulating loss-in-weight powder dosing system with a powder dosing rate of 20 kg/h and with a total of 2.6 kg of an 26.2% aqueous carbohydrate binder solution, and otherwise as described in PCT WO 89/08695, Example 1.

The granulate was finally dried to a water content below 1% and sieved to obtain a product with particle range 300 - 900 µm.

EXAMPLE 9

10 kg of SAVINASE® granulate with particle range between 300 µm and 1000 µm produced as described in US 4,106,991, Example 1, except that it was based on sodium sulphate, was coated with 10% of hydrogenated tallow and 30% of kaolin, as described in Example 6.

A granulate with an inner core containing the proteolytic enzyme SAVINASE® and an outer shell containing a chlorine scavenger, whereby the core and the shell was separated by a protective layer was produced in the following manner.

10 kg of the tallow coated SAVINASE®-containing granulate was transferred to a Lödige mixer FM 50 at 60°C and kept at this temperature during the layering process by use of 60°C hot water in the mixer heating jacket.

9.2 of shell material with the composition

6.8 kg ammonium sulphate
1.0 kg fibrous cellulose, Arbocel BC200
0.2 kg titanium dioxide
0.7 kg kaolin, Speswhite ECC
0.5 kg carbohydrate binder

was supplied with a continuous self-regulating loss-in-weight powder dosing system with a powder dosing rate of 50 kg/h and with a total of 2.1 kg of a 34.7% aqueous carbohydrate binder solution (the binder solution has been slightly acidified with 0.7% citric acid to suppress ammonia evaporation/smell during the granulation). Otherwise the layering was applied as described in PCT WO 89/08695, Example 1.

The granulate was finally dried to a water content below 1% and sieved to obtain a product with particle range 300 - 1000 µm.

EXAMPLE 10

10 kg of SAVINASE® granulate with particle range between 300 µm and 1000 µm produced as described in US 4,106,991, Example 1, except that it was based on sodium sulphate, was coated with 5% of hydrogenated tallow and 15% of kaolin, as described in Example 6.

A granulate with an inner core containing the proteolytic enzyme SAVINASE® and an outer shell containing a chlorine scavenger, whereby the core and the shell was separated by a protective layer, was produced in the manner described in Example 9.

EXAMPLE 11

10 kg of SAVINASE® granulate with particle range between 300 µm and 1000 µm produced as described in US 4,106,991, Example 1, except that it was based on sodium sulphate, was coated with 3% of hydrogenated tallow and 10% of kaolin, as described in Example 6.

A granulate with an inner core containing the proteolytic enzyme SAVINASE® and an outer shell containing a chlorine scavenger, whereby the core and the shell was separated by a protective layer, was produced in the manner described in Example 9.

EXAMPLE 12

10 kg of ALCALASE® granulate with particle range between 300 µm and 1000 µm, produced as described in US 4,106,991, Example 1, except that it was based on sodium sulphate, was coated with 5% of hydrogenated fatty acid (melting point 58°C) and 16% of kaolin as described in Example 6.

A granulate with an inner core containing the proteolytic enzyme ALCALASE® and an outer shell containing a chlorine scavenger, whereby the core and the shell was separated by a protective layer, was produced in the following manner.

10 kg of the tallow coated ALCALASE® containing granulate was transferred to a Lödige mixer FM 50 at 60°C and kept at this temperature during the layering process by use of 60°C hot water in the mixer heating jacket.

9.2 of shell material with the composition

7.0 kg ammonium sulphate
1.0 kg fibrous cellulose, Arbocel BC200
0.7 kg kaolin, Speswhite ECC
0.5 kg carbohydrate binder

was applied as described in Example 9.

The granulate was finally dried to a water content below 1% and sieved to obtain a product with particle range 300 - 1000 µm.

Washing experiments with granulates from Examples 9, 10 and 11

Test:	Wash test with granulates containing chlorine scavengers.	
Principle:	Terg-o-tometer, 100 rpm.	
Water:	6° dH (33% tap water, 67% deionized water)	
Temperature:	40°C	
Time:	15 min. After 15 min. wash, $Na_2S_2O_3$ is added to all the beakers (during a time period of 14 min). Then the swatches are rinsed.	
Detergent:	1 g/l US base powder	
pH:	measured to: 9.2	
Textile/liquid ratio:	8 swatches/800 ml (the dimensions of each swatch is 7 x 7 cm)	
Rinsing:	10 + 15 min. in running tap water	
Test material:	Prerinsed grass on cotton	
Enzymes:	Savinase® (Ref)	7.04 KNPU(S)/g
	Savinase granulates, Ex. 9	3.84 -
	Savinase granulates, Ex. 10	4.40 -
	Savinase granulates, Ex. 11	4.61 -
Enzyme dosage:	0 - 0.09 KNPU/l	
Hypochlorite dosage:	0 - 4.5 - 9.0 ppm NaOCl	
Repetitions:	2 independent repeats	
Analysis:	% remission at 460 nm on Elrepho 2000 (+ UV)	
Comments:	The detergent is dissolved and heated to 40°C in the Terg-o-tometer. NaOCl, enzyme and test swatches are added in the order indicated within 60 seconds.	

Results:

Enzyme	dosage KNPU/l	NaOCl ppm	%R	Δ R
-	0	0	83.4	
Savinase	0.09	0	101.4	18.0
Ex. 9	0.09	0	101.6	18.2
Ex. 10	0.09	0	101.4	18.0
Ex. 11	0.09	0	101.4	18.0
-	0	4.5	85.9	
Savinase	0.09	4.5	93.4	7.5
Ex. 9	0.09	4.5	102.5	16.6
Ex. 10	0.09	4.5	102.4	16.5
Ex. 11	0.09	4.5	102.0	16.1
-	0	9	87.3	
Savinase	0.09	9	87.6	0.3
Ex. 9	0.09	9	94.7	7.4
Ex. 10	0.09	9	89.9	2.6
Ex. 11	0.09	9	88.9	1.6

Comments

With no hypochlorite dosage practically exactly the same enzyme performance from the 4 granulates is observed, measured by Δ R. At a dosage of 4.5 ppm hypochlorite the performance of the Savinase® reference is reduced to approximately half the performance, measured by Δ R, while the three granulates from the examples still exhibit maximal performance. At the high dosage of hypochlorite no significant enzyme performance is observed in relation to the reference. The granulate from Example 9 still exhibits approx. 50% performance due to the high dosage of tallow which delays the release rate, combined with the chlorine scavenging agent.

CLAIMS

1. Detergent additive granulate comprising a core with a primary detergent additive surrounded by a shell comprising a secondary detergent additive, a binder, and granulating agents, and optionally a filler, and a protective coating between the core and the shell, whereby the shell comprises cellulose fibres or artificial fibres, preferably in an amount of between 1.5 and 40% by weight of the shell, more preferably between 5 and 20% by weight of the shell, and whereby the core facultatively comprises cellulose fibres or artificial fibres, preferably in an amount of between 1.5 and 40% by weight of the core, more preferably between 5 and 20% by weight of the core.

2. Granulate according to Claim 1, wherein the core is of a shape corresponding to a maximum ratio between the largest and the smallest dimension of around 3, preferably around 2, more preferably around 1.5.

3. Granulate according to Claims 1 - 2, wherein the amount of the core is between 5 and 85% by weight, preferably between 10 and 50% by weight of the granulate, most preferably between 15 and 40% by weight of the granulate.

4. Granulate according to Claims 1 - 3 wherein the core has a mean particle size between 100 and 1000 µm, preferably 200-700 µm.

5. Granulate according to Claims 1 - 4, wherein the core or the shell contains an enzyme.

6. Granulate according to Claims 1 - 5, wherein the enzyme is a protease, an amylase, a lipase, an amidase, a cellulase, and/or an oxidase.

7. Granulate according to Claims 1 - 6, wherein the filler consists of or comprises inorganic salts.

8. Granulate according to Claims 1 - 7, wherein the shell is surrounded by a final dust suppressing coating.

9. Granulate according to Claims 1 - 8, wherein the protective coating is a mixture of a mono- and diglyceride of a fatty acid.

10. Granulate according to Claims 1 - 9, wherein the protective coating contains an antioxidant.

11. Method for production of the detergent additive granulate according to Claims 1 - 10, which method comprises the introduction of the core into a granulating drum, whereafter sequentially the protective coating agent, the shell material, and optionally a final dust suppressing coating agent, and furthermore cellulose fibres or artificial fibres in the appropriate amounts and at the appropriate stages, are introduced into the granulating device.

INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 90/00043

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 11 D 3/386

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 11 D; C 12 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	US, A, 4740469 (NISHINAKA ET AL) 26 April 1988, see the whole document	1-11
A	EP, A2, 0286773 (ECOLAB INC.) 19 October 1988, see the claims	1-11
P,X	EP, A2, 0304332 (NOVO INDUSTRI A/S) 22 February 1989, see page 2, line 13 - line 19; page 2, line 28 - line 34; page 3, line 58 - line 60; page 4, line 6 - line 8 the claims	1-11

* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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IV. CERTIFICATION

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23rd May 1990	1990 -06- 01
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 90/00043

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 90-05-07
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